

Enhancement of coil-stretch hysteresis by self-concentration in polymer solutions

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Abstract

Coil-stretch hysteresis in extensional flows of dilute polymer solutions is shown to be strongly enhanced as concentration c increases towards c^* , the critical overlap concentration. Large transverse fluctuations within the window of extension rates where hysteresis occurs cause greater intermolecular overlap between partially stretched molecules than at equilibrium. Hydrodynamic screening thus sets in at values of $c/c^* \ll 1$ for such chains, increasing their mean frictional coefficient and allowing for stretched states to be sustained at very low extension rates. Hysteresis progressively diminishes beyond c^* , and vanishes altogether when the crossover from Zimm to Rouse dynamics is complete. The concentration dependence of the width of the hysteresis window is thus non-monotonic, with a large maximum at $c/c^* = 1$.

The dynamics of flexible polymers in a dilute solution are determined by the interplay between forces arising from thermal fluctuations, and intramolecular free-energy and hydrodynamic interactions. This is embodied in the relationship $\lambda_Z = \zeta_Z/4H_0$ between the characteristic “Zimm” relaxation time λ_Z , the friction coefficient ζ_Z of isolated polymer coils at equilibrium and the average stiffness H_0 of the internal resistance of equilibrium coils to stretching. The latter in turn is related to the equilibrium end-to-end distance R_0 : $H_0 = 3k_B T/R_0^2$, where T is the absolute temperature of the solution and k_B denotes the Boltzmann constant. The seminal work of De Gennes [1], Hinch [2] and Tanner [3] suggested that in flows with a dominant extensional component, a sharp coil-to-stretch transition occurs for long molecules when the extensional rate $\dot{\epsilon}$ is such that the Weissenberg number $Wi \equiv \dot{\epsilon}\lambda_Z$ exceeds a critical value $Wi_{c-s} = 1/2$, and molecules unravel and stretch significantly in the flow. The existence of this transition has been beautifully demonstrated in single-molecule experiments [4] and is now thought to play an important role in a number of complex flows of dilute polymer solutions [5; 6].

Both the molecular stiffness H and friction coefficient ζ are in general functions of molecular conformation. In a solution close to its Θ -state where the effects of excluded volume interactions are negligible, molecular resistance to stretching has entropic origins. Although for small deformations this entropic resistance is linear in molecular stretch and the stiffness $H \sim H_0$, it diverges as the end-to-end distance R approaches the contour length L [7; 8]. Intramolecular hydrodynamic interactions result in an increase in ζ with R , from ζ_Z at equilibrium towards the value given by Batchelor’s result for isolated slender rods [9]. As a consequence of the non-linearities in conformation dependence of H and ζ , the coil-stretch transition in extensional flows is associated with strong hysteretic effects [1–3]. The steady state in an extensional flow is primarily the result of a balance between internal entropic resistance to stretching and frictional drag forces exerted by the flowing solvent, which effectively occurs when $\zeta \dot{\epsilon} = 2H$. In very weak flows, this balance is achieved at $R \gtrsim R_0$, and when $Wi > Wi_{c-s}$, only highly stretched states ($R \lesssim L$) are stable. Within a range of extension rates such that $Wi_{s-c} < Wi < Wi_{c-s}$ however, both the coiled and stretched states are stable, and it is possible to kinetically trap molecules in either of these stable states depending on initial conditions [1]. The lower bound of the hysteresis window Wi_{s-c} can be interpreted as a critical strain rate for an ensemble of stretched molecules to transition to the coiled state. Single molecule experiments and simulations [10; 11] and rheological measurements

[12] have confirmed the existence of this window.

It is known that in a dilute solution, the size of the hysteresis window measured in terms of the ratio Wi_{c-s}/Wi_{s-c} is proportional to ratio of ζ_s , the drag coefficient of a nearly fully stretched molecule, to the coiled-state friction ζ_Z . In a concentrated polymer solution on the other hand, it is expected that conformational dependence of the friction coefficient vanishes since interpenetration of molecules completely screens out solvent-mediated hydrodynamic interactions. The behaviour of any single molecule is “Rouse-like” as opposed to the “Zimm-like” dynamics of isolated chains in dilute solutions [8; 13]. Both coiled and stretched molecules have the same Rouse friction coefficient ζ_R in a concentrated solution, and hence no coil-stretch hysteresis is expected in this case.

The objective of this Letter is to show that as the concentration c is increased past the critical value c^* at which equilibrium coils begin to overlap, the change in the width of the coil-stretch hysteresis window with the ratio c/c^* may not be monotonic, but attains a maximum when $c/c^* \sim 1$. The strong enhancement of hysteresis with concentration occurs for $c/c^* \ll 1$, that is, at concentrations that would conventionally place solutions well in the dilute regime.

Recent experiments [16] and molecular simulations have demonstrated that the behaviour of even very dilute polymer solutions in strongly stretching flows can exhibit non-trivial concentration dependence. Some insight into the origin of this “self-concentration” phenomenon can be obtained from single-molecule simulations. Conventionally, the critical overlap concentration is defined as $c^* \equiv d_0^{-3}$, where d_0 is the size of isotropic coils at equilibrium, estimated here as $d_0 = R_0/\sqrt{3}$. Interpreting c as a number density of polymer molecules in solution, the fractional volume pervaded by isotropic coils at equilibrium is $cd_0^3 = c/c^*$. In extensional flows within the coil-stretch hysteresis window, conformational fluctuations of size d transverse to the principal stretching axis are large and comparable in magnitude to equilibrium fluctuations d_0 since $Wi < 1$ (Fig. 1 a) within the window. Therefore, the pervaded volume ℓd^2 of a molecule in its stable, stretched state with an average length $\ell \gg R_0$ along the principal direction of extension is much larger than at equilibrium (Fig. 1 b). The volume fraction pervaded by stretched molecules,

$$\phi = c \ell d^2 = \frac{c}{c^*} \frac{\ell}{d} \left(\frac{d}{d_0} \right)^3. \quad (1)$$

Thus, when aspect ratio $\ell/d \gg 1$ but with transverse fluctuations $d/d_0 \sim O(1)$, a solution may

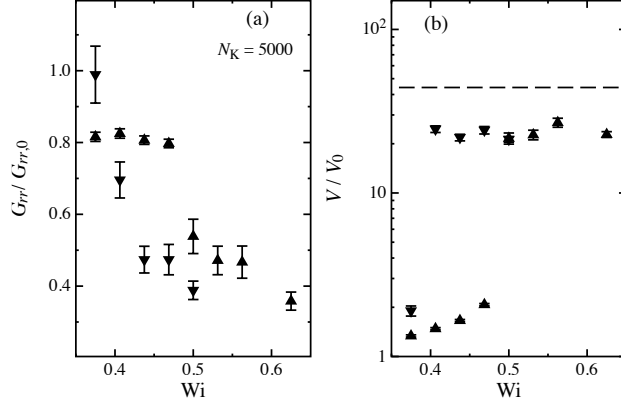


FIG. 1. (a) Results of Brownian-dynamics simulations [14; 15] for gyration tensor component G_{rr} of isolated chains transverse to the direction of stretching in steady uniaxial extensional flows; (b) mean pervaded volume in simulations of isolated linear bead-spring chains: the volume V is estimated from components of the gyration tensor \mathbf{G} as $V = G_{rr} \sqrt{G_{zz}}$, and V_0 is the equilibrium volume of isotropic coils. Coil-stretch hysteresis is observed for $Wi < 0.5$; chains initially at equilibrium (\blacktriangle) and chains initially stretched to 90% maximum permissible length (\blacktriangledown) have different quasi-steady-states. The horizontal dashed line in (b) indicates the volume estimate assuming $G_{zz} = L^2/12$ (valid for rods of length L) and $G_{rr} = G_{rr,0}/2$.

initially be very dilute at equilibrium with $c/c^* \ll 1$, but ϕ could be significantly larger in an extensional flow in the vicinity of the coil-stretch transition. Intermolecular interactions can be more significant than at equilibrium and it is even possible that partially stretched coils may overlap, as observed recently in multi-chain simulations [17]. The question is: how does self-concentration affect the dependence of the friction coefficient ζ on molecular stretch?

As already mentioned, in the limit of infinite dilution, the rod-like friction coefficient ζ_r of stretched molecules of length ℓ and diameter d can be estimated from the theory for suspensions of slender rods [9] as $\zeta_r/\zeta_z \sim (\ell/d_0)/\ln(\ell/d)$. For non-zero c , the average distance between stretched molecules $h = (c\ell)^{-1/2}$, and when $d/h = \phi^{1/2} \ll 1$, far-field hydrodynamic interactions modify the friction coefficient, and approximately for non-overlapping chains when the instantaneous $\phi \ll 1$ [9],

$$\frac{\zeta_r}{\zeta_z} \sim \frac{1}{\ln(\ell/d) - \ln(1 + \ell/h)} \frac{\ell}{d_0}. \quad (2)$$

To the best of this author's knowledge, a theory for a solution of anisotropic chains near and beyond overlap has not been developed. We can nevertheless draw upon current understand-

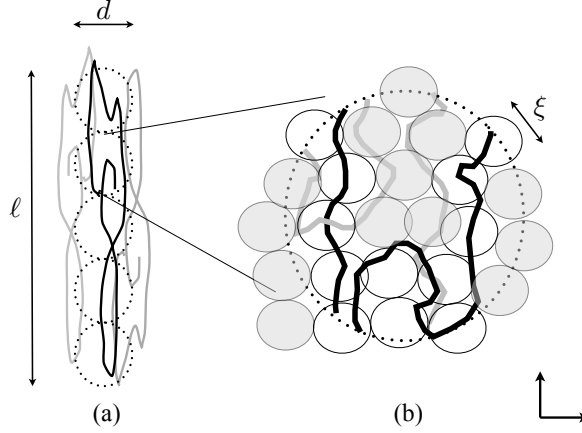


FIG. 2. Schematic of length-scales in a solution of partially unravelled, overlapping polymer chains aligned along the principal stretching direction in a uniaxial extensional flow: each chain consists of (a) $N_d = \ell/d$ domains of size determined by transverse fluctuations, and (b) N_h correlation blobs of size ξ_h .

ing of the Zimm-to-Rouse crossover for isotropic coils [8; 13; 18]. In a solution consisting of partially stretched chains all oriented along the axis of extension, progressive screening of hydrodynamic interactions with increasing overlap is described in terms of a hydrodynamic screening length $\xi_h < d$ such that intramolecular hydrodynamic interactions persist only at length scales smaller than ξ_h , but are screened at larger length scales. Therefore, each molecule on average acts as a Rouse chain of N_h “blobs”, each of size ξ_h (Fig. 2) [13; 18]. The quantities ξ_h and N_h are determined by firstly noting that ξ_h is the scale at which segments in any chain first encounter those from neighbouring chains; hence $c \xi_h^3 N_h = 1$. Secondly, assuming that chain segments at length scales smaller than d retain a spatial distribution similar to the ideal random-walk at equilibrium, and $\xi_h^2/d^2 = (N_K/N_h)(N_K/N_d) = N_d/N_h$ where $N_K \equiv L^2/R_0^2$ is the number of Kuhn segments in the molecule, and $N_d = \ell/d$ is the instantaneous aspect ratio (Fig. 2). Therefore, when $\phi \geq 1$, $\xi_h/d = \phi^{-1}$ and $N_h = \phi^2 (\ell/d)$, and the total Rouse-like friction coefficient is

$$\frac{\zeta_r}{\zeta_Z} = \frac{\xi_h}{d_0} N_h = \phi \frac{\ell}{d_0} = \frac{c}{c^*} \left(\frac{\ell}{d_0} \right)^2 \left(\frac{d}{d_0} \right)^2. \quad (3)$$

In the regime of intermediate values of $0.01 < \phi < 1$, a simple linear interpolation is used between the estimates given by Eqns. (2) and (3) above for ζ_r/ζ_Z [15]. The friction of equilibrium coils ζ_c also increases with c/c^* from the value for isolated coils ζ_Z , firstly due to

far-field hydrodynamic interactions when $c/c^* < 1$, and then due to screening when $c/c^* > 1$. For the sake of simplicity, changes ζ_c before overlap are neglected; that is, it is assumed that $\zeta_c = \zeta_Z$ when $c/c^* \leq 1$. Beyond overlap, accounting for screening as outlined above gives

$$\frac{\zeta_c}{\zeta_Z} = \frac{c}{c^*}. \quad (4)$$

Screening is considered to be complete when either ζ_r or ζ_c attain the value corresponding ζ_R . Therefore, they are limited in the model here to the maximum value set by $\zeta_R/\zeta_Z = (b_K/d_0) N_K = \sqrt{3N_K}$, where $b_K \equiv R_0^2/L$ is the Kuhn length. Equation. (3) suggests that for stretched chains $\zeta_r = \zeta_R$ at a concentration c^\dagger such that

$$\frac{c^\dagger}{c^*} = \sqrt{3N_K} \left(\frac{\ell}{d_0} \right)^{-2} \left(\frac{d}{d_0} \right)^{-2}, \quad (5)$$

whereas for coiled molecules the Zimm-to-Rouse crossover is complete at a $c^{\dagger\dagger}/c^* = \zeta_R/\zeta_Z = \sqrt{3N_K}$. In other words, not only is the crossover for stretched chains complete at $c^{\dagger\dagger} \ll c^\dagger$, but if $\ell \sim L$ and $(d/d_0)^2 \sim O(1)$, the crossover occurs at $c^{\dagger\dagger}/c^* \sim N_K^{-1/2} \ll 1$, well within the dilute regime for solutions of long molecules.

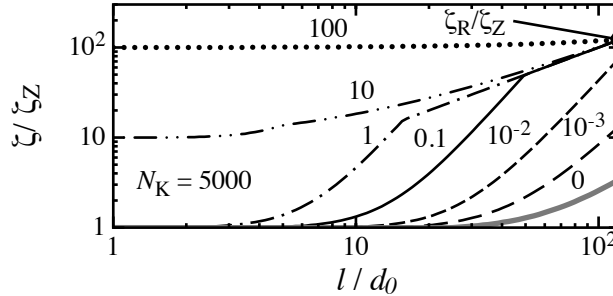


FIG. 3. Variation of friction coefficient ζ with molecular stretch ℓ at fixed transverse chain dimensions $(d/d_0)^2 = 0.5$: the numbers alongside curves indicate c/c^* . The maximum value for the friction coefficient ζ_R/ζ_Z and the maximum permissible length ℓ/d_0 are both equal to $\sqrt{3N_K}$.

The mean friction coefficient ζ is calculated here using a linear mixing rule to interpolate between ζ_r and ζ_c depending on polymer stretch [15]; Fig. 3 shows the variation of ζ with molecular stretch for c/c^* values ranging from the limit of infinite dilution to nearly c^\dagger/c^* when the transverse dimensions are held fixed such that $(d/d_0)^2 = 1/2$. The friction coefficient ζ_s for hypothetical transversely bloated, fully-stretched chains with $\ell = L$ is much stronger than that of ζ_c when $c < c^{\dagger\dagger}$. The ratio ζ_s/ζ_c becomes independent of concentration when

$c^{\dagger} < c < 1$ since both $\zeta_s = \zeta_R$ and $\zeta_c = \zeta_Z$ are constant. Above c^* , the ratio ζ_s/ζ_c decreases with c as ζ_c “catches up” with ζ_s , and beyond c^\dagger , $\zeta_s/\zeta_c = 1$.

Predictions for coil-stretch hysteresis are obtained with a mean-field conformation-tensor model whose dynamical equations for the evolution of the axial (zz) and transverse (rr) components of the conformation tensor \mathbf{M} are [19]:

$$\frac{dM_{zz}}{dt} = 2\dot{\epsilon} M_{zz} - \frac{4H}{\zeta} M_{zz} + \frac{4k_B T}{\zeta}, \quad (6)$$

$$\frac{dM_{rr}}{dt} = -\dot{\epsilon} M_{rr} - \frac{4H}{\zeta} M_{rr} + \frac{4k_B T}{\zeta}. \quad (7)$$

The model consistently accounts for the effects of thermal fluctuations and flow, along with conformation-dependent molecular friction and entropic stiffness. Here, $H = H_0(1 - 1/N_K)[1 - (M_{zz} + 2M_{rr})/L^2]^{-1}$ is the nonlinear effective stiffness of the resistance to stretching, and the friction coefficient ζ is calculated as described above [15] after identifying the instantaneous ℓ and d of partially stretched coils with $M_{zz}^{1/2}$ and $M_{rr}^{1/2}$, respectively. The near-equilibrium relaxation time $\lambda_0 = \zeta_c R_0^2/(12k_B T)$, so that $\lambda_0 = \lambda_Z$ when $c/c^* \leq 1$, and varies as ζ_c for concentrations above c^* . The polymer contribution to the extensional viscosity, $\bar{\eta}_p = cH(M_{zz} - M_{rr})/\dot{\epsilon}$. On rescaling model equations with R_0 and λ_0 as the characteristic length and time scales, the sole dimensionless model parameters are N_K , c/c^* and the Weissenberg number, $Wi = \dot{\epsilon}\lambda_0$.

Unlike the results shown in Fig. 3, the hysteresis predictions in Fig. 4 are with the transverse size d/d_0 of chains consistently determined at every Wi by the dynamics in Eq. (7). It is observed that for $N_K = 5 \times 10^3$, hysteresis windows widen first with increasing concentration in the dilute regime (Fig. 4 (a)) until about $c/c^* \sim 0.1$, after which a decrease in window size commences only beyond c^* , with hysteresis vanishing completely at $c/c^* \sim 100$ (Fig. 4 (b)). The non-monotonic concentration dependence of Wi_{c-s}/Wi_{s-c} is shown in Fig. 5, which compares well with the estimate ζ_s/ζ_c calculated *a priori* with the assumption of constant $d/d_0 = 1/\sqrt{2}$.

Although the discussion above is for solutions close to the Θ -state, similar arguments are expected to hold when excluded-volume interactions are important. Indeed, the self-concentration effect may be marginally greater because the hysteresis window size at infinite dilution (horizontal line in Fig. 5) is smaller in good solvents and may even vanish completely [21; 22], but ζ_R (and hence the maximum in Fig. 5) is expected to be unaffected by solvent quality. An analysis of the dependence of the scaling exponents shown in Fig. 5 on solvent

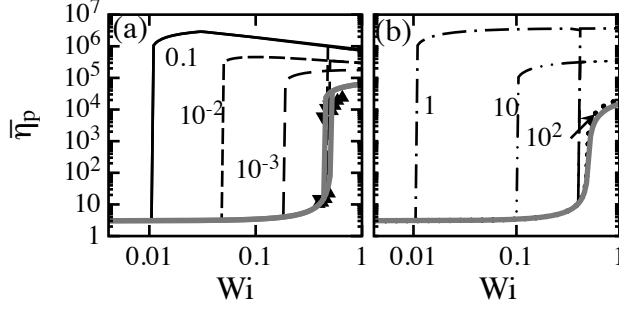


FIG. 4. Predictions of the conformation-tensor model for coil-stretch hysteresis in $\bar{\eta}_p$, the polymer contribution to steady-state extensional viscosity (scaled by $c k_B T \lambda_0$), shown for the sake of clarity separately for (a) $c/c^* < 1$, and (b) $c/c^* \geq 1$; the numbers alongside curves indicate c/c^* values. Symbols shown in (a) are data for the window predicted by Brownian dynamics simulations (details shown separately in [15]). The thick gray curves in (a) are predictions obtained with the model in the infinite-dilution limit, while that in (b) is the prediction by the (FENE-P) model [20] with Rouse-like conformation-independent $\zeta = \zeta_c$.

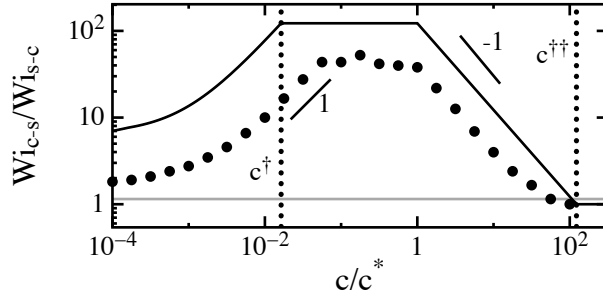


FIG. 5. Concentration-dependence of the width of the coil-stretch hysteresis window: symbols are predictions of the conformation tensor model. The horizontal line is the width predicted in the infinite-dilution limit, while the curve bounding the symbols from above is estimated by the ratio ζ_s/ζ_c , with ζ_s being calculated from data in Fig. 3 for fully-stretched chains with large transverse fluctuations, that is $\ell = L$, and $(d/d_0)^2 = 1/2$.

quality requires consideration of the changes in H with solvent quality [22; 23] which is beyond the scope of this Letter.

There appears to be indirect experimental evidence for the predictions above from measurements of the characteristic time-scale of radial decay in exponentially thinning slender filaments of dilute polymer solutions. This relaxation time has been shown in simulations

to be proportional to the ratio Wi_{cs}/Wi_{sc} [24], while Clasen *et al.* [16] have experimentally observed that it is strongly enhanced with concentration even for solutions with $c/c^ast \ll 1$. Firm confirmation may be obtained by more systematic rheological measurements [12] and by visualizing stained molecules in extensional flows [10]. The predictions may further be tested in simulations of multiple hydrodynamically interacting chains in elongational flows with appropriate periodic boundary conditions [17]. Such studies will also throw light on dynamical hydrodynamic and excluded volume screening in the dilute-to-concentrated solution crossover in polymer solutions. This understanding is critical to many applications such as turbulent drag reduction, ink-jet printing *etc.* where small quantities of polymeric additives are employed to induce large elastic stresses in the fluid in flows with significant extensional components.

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Supplementary material for “Enhancement of coil-stretch hysteresis by self-concentration in polymer solutions”

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I. CONFORMATION- AND CONCENTRATION-DEPENDENT FRICTION COEFFICIENT

The friction coefficient ζ of partially unravelled and partially aligned chains at any concentration is anticipated to lie between the value ζ_c for isotropic coils at the same concentration at equilibrium, and an estimate ζ_r derived assuming that chains are slender rod-like objects of average length ℓ and d , all aligned in the principal stretching direction in a flow. A simple linear “mixing rule” is used for ζ , interpolating between ζ_c and ζ_r as follows:

$$\frac{\zeta}{\zeta_Z} = \frac{\zeta_r}{\zeta_Z} \frac{\ell - \ell_0}{L - \ell_0} + \frac{\zeta_c}{\zeta_Z} \frac{L - \ell}{L - \ell_0}, \quad (1)$$

where ζ_Z is the limiting (“Zimm”) value for isolated coils at equilibrium, and L is the polymer contour length.

Three distinct concentration regimes can be identified for modeling ζ_r/ζ_Z depending on the instantaneous pervaded volume fraction of stretched molecules:

$$\phi = c \ell d^2 = \frac{c}{c^*} \frac{\ell}{d} \left(\frac{d}{d_0} \right)^3, \quad (2)$$

where c is the molecular number density, c^* is the conventional definition of the critical overlap concentration, which is estimated here as $c^* = d_0^{-3}$ for isotropic coils of diameter $d_0 = R_0/\sqrt{3}$ at equilibrium; R_0 is the root-mean-squared end-to-end distance at equilibrium.

A. ζ_r/ζ_Z in dilute regime, $\phi \leq 10^{-2}$

For non-overlapping chains, the mean transverse separation h is such that $c \ell h^2 = 1$, and hence from Eqn. (2),

$$\frac{h}{d} = \frac{1}{\sqrt{\phi}}. \quad (3)$$

The following approximation is based on Batchelor’s [1] results for suspensions of slender rods:

$$\frac{\zeta_r}{\zeta_Z} = \frac{K}{K + \ln F} \left(\frac{\ell}{d_0} \right), \quad (4)$$

where the argument of the logarithmic correction in the denominator is

$$F = \begin{cases} \frac{\ell/d}{1 + \ell/h} = \frac{\ell/d}{1 + (\ell/d)\sqrt{\phi}}, & \text{if } \ell/d > 1 + \ell/h \\ 1. & \text{if } \ell/d \leq 1 + \ell/h \end{cases} \quad (5)$$

With this, $\zeta_r \rightarrow \zeta_Z$ as $\ell \rightarrow d_0$, and for $\ln F \gg K$,

$$\frac{\zeta_r}{\zeta_Z} = \frac{K}{\ln(\ell/d) - \ln(1 + \ell/h)} \frac{\ell}{d_0}. \quad (6)$$

The conditional specification of F in Eqn. (5) avoids singular behaviour as the aspect ratio ℓ/d unity in the limit of infinite dilution, $\phi \rightarrow 0$; the choice of $F = 1$ is only needed for $\ell/d \approx 1$ which typically occurs near equilibrium, where the mixing rule in Eqn. (1) ensures that ζ_r is of little consequence. The constant $K = 0.15$ is chosen to qualitatively match the hysteresis in steady-state extensional viscosity predicted by Brownian dynamics simulations in the infinite dilution limit (see Fig. 2 below). The approximation in Eqn. (6) is expected to be valid when $h/d \gg 1$ or $\sqrt{\phi} \ll 1$ [1]. Therefore, Eqns. (4) and (5) are used when $\sqrt{\phi} \leq 0.01$.

B. ζ_r/ζ_Z in non-dilute regime, $\phi \geq 1$

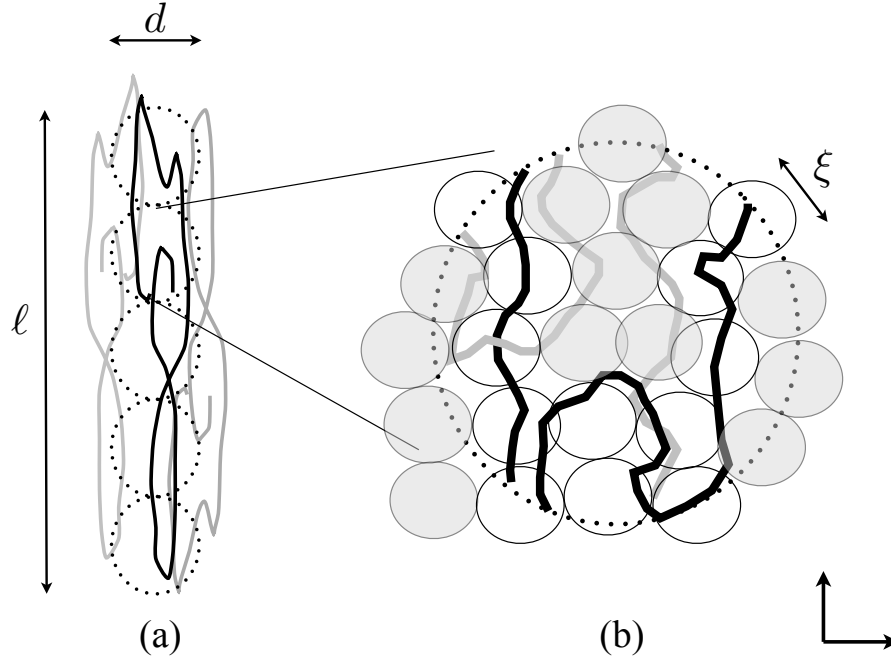


FIG. 1 Schematic of length-scales in a solution of partially unravelled, overlapping polymer chains aligned along the principal stretching direction in a uniaxial extensional flow

Each molecule is a chain of $N_d = \ell/d$ “beads”. Within each bead are correlation blobs [2; 3] of size ξ , with a total of N_h blobs along the chain. Intramolecular hydrodynamic interactions are restricted to segments within a blob, but are screened at larger length

scales. The hydrodynamic screening length ξ_h is that at which the intramolecular segmental density is equal to the average segmental density of the solution as a whole, which in turn implies that blobs of all molecules span the solution volume or

$$c N_h \xi_h^3 = 1. \quad (7)$$

Assuming that an equilibrium-like structure survives at length scales smaller than the size of the transverse fluctuations d when $Wi \lesssim O(1)$, for solutions near the Θ -state,

$$\frac{\xi_h^2}{d^2} = \frac{N_K/N_h}{N_K/N_d} = \frac{\ell/d}{N_h}, \quad (8)$$

where $N_K \equiv L^2/R_0^2$ is the number of Kuhn segments. The rod-like mean friction coefficient of the partially-stretched chain chain is calculated as the Rouse drag of N_h blobs, each with a Zimm friction $\zeta_\xi = (\xi_h/d_0) \zeta_Z$,

$$\frac{\zeta_r}{\zeta_Z} = \frac{\xi_h}{d_0} N_h = \phi \frac{\ell}{d_0}, \quad (9)$$

C. ζ_r/ζ_Z in transition regime, $0.01 < \phi < 1$

Since screening sets in at incipient overlap, from Eqn. (9) above

$$\frac{\zeta_r}{\zeta_{c,Z}} = N_d \frac{d}{d_0} = \frac{\ell}{d_0}, \quad \text{at } \phi = 1. \quad (10)$$

For a given c/c^* , and given ℓ and d , if ϕ as calculated by Eqn. (2) is in the transition regime, ζ_r is calculated by linearly interpolating in ϕ between the value calculated above at $\phi = 1$, and that calculated using Eqn. (4) with $\phi = 0.01$; that is,

$$\frac{\zeta_r}{\zeta_Z} = \left[\frac{K}{K + \ln F|_{\phi=0.01}} \frac{1-\phi}{1-0.01} + \frac{\phi-0.01}{1-0.01} \right] \frac{\ell}{d_0}. \quad (11)$$

D. Concentration dependence of ζ_c/ζ_Z

The variation of ζ_c of equilibrium coils due to intermolecular hydrodynamic interactions in the dilute regime as c increases towards c^* is not well studied. Beyond c^* , the effects of hydrodynamical screening and crossover in dynamical properties in the linear response regime (*e.g* diffusivity) have been well documented [3]. These observations suggest that the

variation in ζ_c with concentration may be approximated as follows:

$$\frac{\zeta_c}{\zeta_Z} = \begin{cases} 1, & \text{if } c \leq c^*, \\ \frac{c}{c^*}, & \text{if } c > c^*, \end{cases} \quad (12)$$

the second result following from applying blob arguments for equilibrium coils.

As noted in the main body of the paper, screening is considered to be complete in either the stretched or coiled states when ζ_c or ζ_c reach the Rouse friction coefficient, estimated as

$$\frac{\zeta_R}{\zeta_Z} = \frac{b_K}{d_0} N_K = \sqrt{3 N_K}, \quad (13)$$

where $b_K \equiv R_0^2/L$ is the Kuhn length.

II. BROWNIAN DYNAMICS SIMULATIONS OF ISOLATED FLEXIBLE POLYMERS

Results of single-molecule Brownian dynamics simulations presented in this study are from Ref. [4]. The molecular model and its parameters, and the simulation algorithm have been reported in Refs. [5; 6]. Briefly, polymer molecules of N_K Kuhn segments are modeled as chains of $N < N_K$ beads connected by Finitely-Extensible Nonlinear Elastic (FENE) springs, and intramolecular hydrodynamic interactions are incorporated through Rotne-Prager-Yamakawa tensors. Excluded-volume interactions are neglected for chains at the Θ -state. Independent trajectories of chains are generated by integrating a stochastic differential equations for bead positions that describe their motion under the combined action of hydrodynamic drag forces exerted by a homogeneous flow of the surrounding solvent and its thermal fluctuations, and intramolecular forces arising from free-energy interactions. The gyration tensor

$$\mathbf{G} \equiv \frac{1}{N} \sum_{\nu=1}^N \langle \mathbf{R}_\nu \mathbf{R}_\nu \rangle, \quad (14)$$

where \mathbf{R}_ν is the position vector of the ν -th bead relative to the center-of-mass of a chain of N beads, and the angular brackets represent averaging over a large ensemble of independent stochastic realizations of chain configurations. The volume pervaded by a chain $V \equiv \sqrt{\det \mathbf{G}}$. In flow, the polymer contribution to the extra-stress $\boldsymbol{\tau}_p$ is given by the Kramers' equation

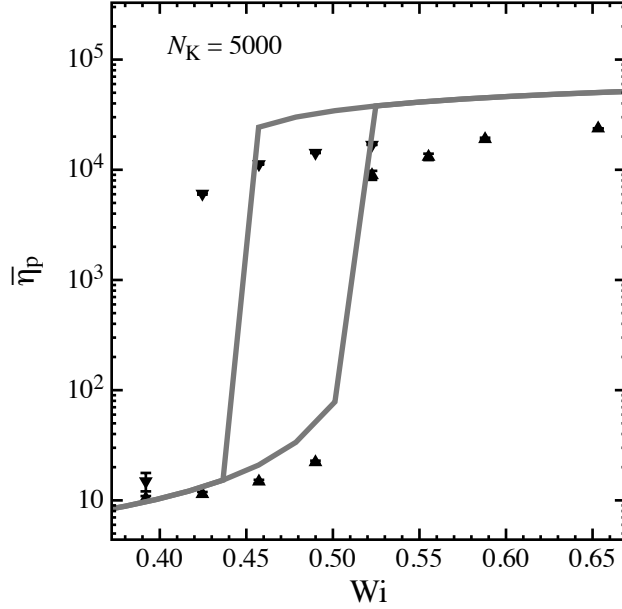


FIG. 2 Coil-stretch hysteresis in steady-state extensional viscosity: symbols are results of Brownian dynamics simulations with isolated 26-bead chains, obtained with initial ensembles consisting of equilibrium coils (\blacktriangle), and consisting of initially stretched chains (\blacktriangledown); continuous curves are predictions of the conformation-tensor model at infinite dilution.

[7], and the extensional viscosity is defined as

$$\bar{\eta}_p \equiv - \frac{\tau_{p,zz} - \tau_{p,rr}}{\dot{\epsilon}}. \quad (15)$$

The evaluation of the longest relaxation time for defining the Weissenberg number Wi is described in Ref. [6]. Predictions of coil-stretch hysteresis are obtained by running to steady-state two separate ensembles with different initial distributions of chain configurations at each strain-rate $\dot{\epsilon}$: results for coiled states are obtained with an initial ensemble at equilibrium, while stretched state simulations start with chains nearly fully extended and all oriented in the z -direction. Figure 2 shows hysteresis in $\bar{\eta}_p$ obtained with simulations, along with predictions of the conformation-tensor model in the limit of infinite dilution, with $K = 0.15$.

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